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NOTE

Improved Preparation of 5-Chloro-2-methoxycarbonyl-1-indanone for Total Synthesis of Indoxacarb

LINGZI ZHANG, JIAFU ZHANG and DEQUN SUN*

Marine College, Shandong University at Weihai, Weihai 264209, P.R. China

*Corresponding author: Tel/Fax: +86 631 5688537; E-mail: dequn.sun@sdu.edu.cn

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5-Chloro-2-methoxycarbonyl-1-indanone **1** is an important intermediate for the synthesis of arthropodicidal oxadiazines indoxacarb. Here a convenient and environmentally friendly method with higher yield and low cost compared to existing method was developed. This method could be useful in manufacturing of indoxacarb, lowering the costs and avoiding excessive pollution.

Key Words: Synthesis, 5-Chloro-2-methoxycarbonyl-1-indanone, Indoxacarb.

Indoxacarb (Fig. 1) is an oxadiazine insecticides developed by American DuPont Company in 1992, registered and listed in 2001.[1] It shows outstanding field activity, low mammalian toxicity, environmental compatibility and a high degree of non-target organism safety[2-5]. Further studies to investigate its insecticidal mechanism and attempts to find a new compound, similar insecticide have recently attracted attention[6-12].

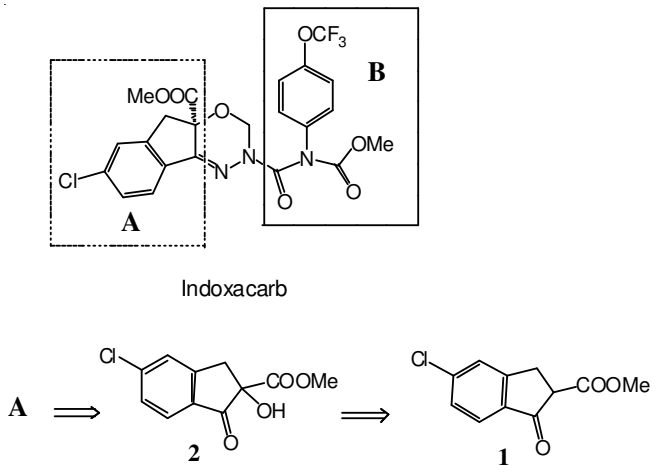

Fig. 1. Structures of indoxacarb and title compound **1**

Indoxacarb and most of its analogues have two important moieties (structure **A** and **B**) to maintain their excellent activity (Fig. 1). In our previous work,[13] the novel preparation of structure **B** with excellent yield was reported. As far as synthesis of structure **A**, the literature[14] reported that incorporation of moiety **A** into indoxacarb molecular can be fulfilled by intermediate **1** (Fig. 2). Starting from Friedel-Crafts reaction, the acylation of chlorobenzene gives compound **3** in 87 % yield. Cyclization of compound **3** catalyzed by concentrated sulphuric acid produces indanone **4** with yield of 70 %. Compound **4** subsequently reacts with dimethyl carbonate to give title intermediate **1** as crude product, which is oxidized directly by *m*-CPBA to afford the precursor **2**, which can be used to build up the oxadiazine cycle in indoxacarb molecule. In this work, the emphasis was focused on developing convenient and environment friendly methods for the preparation of compound **1** from compound **4**.

The melting point was measured with an XRC-1 microscope melting-point apparatus and was not corrected. Dimethyl carbonate and dimethyl formamide was dried over sodium and anhydrous sodium sulfate respectively before use.

Chemical synthesis: To a solution of indanone (**4**) (0.3 g, 80 %, 1.44 mmol) in dimethyl carbonate (DMC) (2 mL, 26.6 mmol) and dimethyl formamide (2 mL) was added sodium hydride (69 mg, 60 % in mineral oil, 1.73 mmol) in three portions at room temperature. After 0.5 h, the reaction mixture was poured into cold 1 M hydrochloric acid. The aqueous phase was extracted with CH_2Cl_2 (3 × 10 mL). The combined organic layers were dried over anhydrous magnesium sulfate, filtered and evaporated in vacuum to obtain an oil, which was purified by silica gel column chromatography to give compound **1** as off-white solid (0.28 g, yield 88 %): m.p.: 79-81 ºC (lit.: 79.2-80.5 ºC[15]).

In existing studies of the preparation of indoxacarb, the 5-chloro-2-methoxycarbonyl-1-indanone (**1**) was obtained by

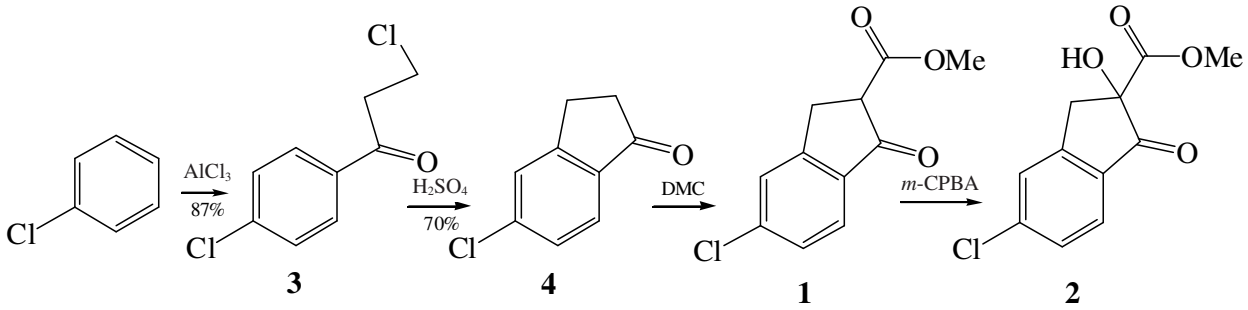

Fig. 2. Synthetic route for 5-chloro-2-methoxycarbonyl-1-indanone (**1**)

three different methods on the whole. In method **I**, several workers reported[15-18] that **1** was obtained by refluxing compound **4** in dimethyl carbonate (DMC) and the dimethyl carbonate was used as both reactant and solvent, the yield of **1** was reached to 76 %[15]. In method **II**, Deng *et al.*[19,20] employed tetrahydrofuran as solvent under refluxing condition with remarkable lower yield (67 %[20]). In method **III**, Duan reported[14] preparation of **1** was fulfilled in dimethyl formamide at room temperature, however, addition sequence was inconvenient and the yield was unclear. To avoid these issues, we present an improved method to prepare 5-chloro-2-methoxycarbonyl-1-indanone **1** from indanone **4** under mild condition with better yield. The contrast between present method and the reported methods was described in Table-1.

TABLE-1
SUMMARY OF THE FOUR SYNTHETIC METHODS

	NaH (eq)	Solvent	Reaction temperature	Reaction time	Yield (%)
Method **I**	2.2	DMC	Reflux	1 h	76
Method **II**	2.0	THF	Reflux	0.5 h	67
Method **III**	2.0	DMF	Room temperature	Over night	Unclear
Our method	1.2	DMC:DMF 1:1(V/V)	Room temperature	0.5 h	88

To accelerate acylation of **4**, the 4-dimethylaminopyridine was used as a carbonyl activator, however, it did not benefit the conversion. Meanwhile, the different equivalent of sodium hydride was examined and optimized. We found the most suitable amount of NaH was 1.2 eq rather than reported 2.2 eq. Furthermore, binary mixed solvent composed of dimethyl formamide and dimethyl carbonate was employed in our methodology, since we found the presence of DMF did do a remarkable contribution to the reaction speed. Therefore, the ratio of DMF:DMC was optimized to 1:1 to afford the best conversion of compound **4** to compound **1** in a short time with yield of 88 %.

Conclusion

In summary, an improved method to prepare the important intermediate **1** for synthesis of indoxacarb was developed. In this methodology, the title compound **1** was obtained with higher yield under mild reaction condition. This finding will be valuable in practical manufacture of indoxacarb, lowering production costs and energy consumption and reducing environmental pollution.

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